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# THE COORDINATION OF SMALL MOLECULES BY MANGANESE(II)

## III *. THE REVERSIBLE BINDING OF CARBON MONOXIDE BY $MnX_2(PR_3)$ ($R_3 = PhMe_2$, $PhEt_2$, $Pr^n_3$; X = Cl, Br, I) IN THE SOLID STATE AND IN SOLUTION

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## Summary

The manganese(II) phosphine complexes $MnX_2(PR_3)$ ($PR_3 = PPhMe_2$, X = Cl, Br, I; $PR_3 = PPhEt_2$, $PPr^n_3$, X = Cl, Br) have been found to react with carbon monoxide in a 1/1 ratio to form "$MnX_2(CO)(PR_3)$" in the solid state and in tetrahydrofuran (THF) solution. The reaction may be reversed either by a pressure drop or a temperature rise, and the gas released is shown to be carbon monoxide by mass spectral methods. The rate of reaction of $MnX_2(PR_3)$ with carbon monoxide appears to be both phosphine and halide dependent. In THF solution ESR measurements indicate that the CO adduct is the pseudooctahedral $MnX_2(THF)_2(CO)(PR_3)$ species, whereas in the solid state it is the pseudotetrahedral $MnX_2(CO)(PR_3)$. The $\nu(CO)$ infrared band appears at 2100–2085 $cm^{-1}$ in the carbon monoxide adducts.

The manganese(II) phosphine complexes, $MnX_2(PR_3)$, are extremely unusual, being able to reversibly bind small molecules under very mild conditions.

$$MnX_2(PR_3) + L \rightleftharpoons MnX_2(PR_3)(L) \qquad L = O_2, CO, NO$$

The reaction with dioxygen has been well studied by us [1,3,4] and, although attempts to isolate suitable crystals of the dioxygen adducts have so far proved unsuccessful, electron spin resonance measurements have indicated that the $Mn{-}O_2$ linkage involves "bent" dioxygen [4]. Although reversible binding of small molecules is observed for $O_2$, CO, and NO we find that sulphur dioxide forms irreversible adducts of unusual stoicheiometry $\{MnX_2(PR_3)\}_3(SO_2)_2$ [2].

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* For part II see Ref. 2.

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We here wish to report our studies of the carbon monoxide adducts of the $MnX_2(PR_3)$ complexes. The facile reversible reaction of CO with transition metal complexes is the basis of a number of catalytic processes such as hydroformylation [5,6]. A member of other reversible systems are known. For example, it has been found that copper(I) iodide in a methanolic solution of ethylenediamine adsorbs CO when the Cu/en ratio is 1/3 and from this has been isolated $[Cu(en)_2(CO)]I$, which exhibits $\nu(CO)$ at 2060 $cm^{-1}$ [7]. Earlier work had identified a carbonyl species for Cu/en ratio of 1/1, and it was possible to decarbonylate this species by application of a vacuum at temperatures greater than 0°C [8]. Reversible coordination of CO has been reported by Osborn and coworkers [9] for the bimetallic $[LCu_2]^{2+}$ (where L = 1,4-bis-(1-oxa-4,10-dithia-7-azacyclododecan-7-ylmethyl)benzene) in both the solid state and in solution. Identical products are obtained if the solid or a nitromethane solution is exposed to CO ($\nu(CO)$ 2070 $cm^{-1}$, in both cases). Decarbonylation could be achieved at 80°C or by bubbling an argon stream through the solution. James et al. have reported [10] reversible coordination of CO by the hexacoordinate complexes $L_2Fe(OMBP)$ (OMBP = octamethyltetrabenzoporphyrin) in toluene solutions. Addition of CO to such solutions resulted in a darkening of the characteristic green solutions and the appearance of a reflected red colouration. The reaction was found to be reversible by prolonged degassing of the solutions or by the addition of excess L. The reversible coordination of CO to bis (3,5-butylcatecholato)vanadium(IV) in methanol and dimethylsulphoxide has recently been reported by Wilshire and Sawyer [11].

## Results and discussion

The $MnX_2(PR_3)$ complexes are easily prepared by the reaction of anhydrous manganese(II) salts with the phosphine in a dry 60/50 toluene/dichloromethane mixture under an inert atmosphere (see Experimental). Once isolated the complexes are indefinitely stable if stored under dry inert conditions. We report here our observations on the quantitative 1/1 reaction of $MnX_2(PR_3)$ ($R_3$ = $PhMe_2$, $PhEt_2$, $Pr^n_3$, X = Cl, Br, I) with carbon monoxide in tetrahydrofuran (THF) and some brief details of the solid isotherms we have sustained. Isolated complexes are listed in Table 1.

It should be mentioned that although the $MnX_2(PR_3)(O_2)$ complexes are highly coloured, the $MnX_2(PR_3)(CO)$ are only very pale yellow/orange and differ only slightly in colour from their decarbonylated analogues.

### *Solution studies*

Absorption of carbon monoxide by THF solutions of the $Mn(PR_3)X_2$ complexes have been quantitatively followed by use of a thermostated gas burette apparatus (see Experimental). Under the conditions of our experiments the volume of CO absorbed by 100 $cm^3$ of THF at 0°C was found to be $0.63 \times 10^{-3}$ mol (Fig. 1). When studying absorption of CO by 100 $cm^3$ solutions of the complexes this volume was subtracted from the total in order to determine the actual volume absorbed by the complex alone. The mole ratio Mn/CO was found to be consistently 1/1 and independent of concentration up to the solubility point of the complex (Fig. 2). Desorption of the carbon monoxide was accomplished by either warming the solutions to ca. 50°C, applying a slight vacuum or by joint temperature/pressure

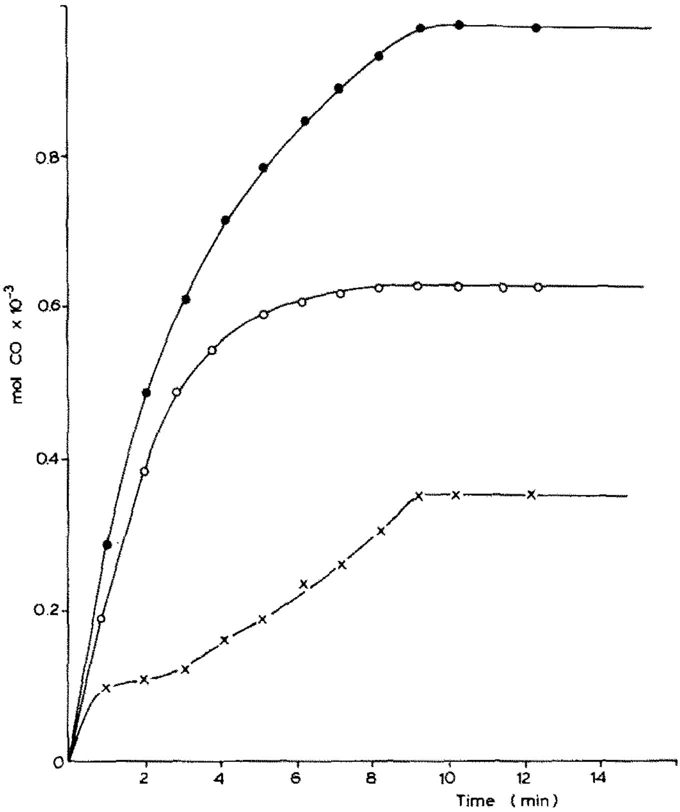


Fig. 1. CO uptake by Mn(PPr$_3$)Cl$_2$ at 0°C (0.35 × $10^{-3}$ mol in 100 ml THF), ⊙ THF; x Complex; ● THF + complex.

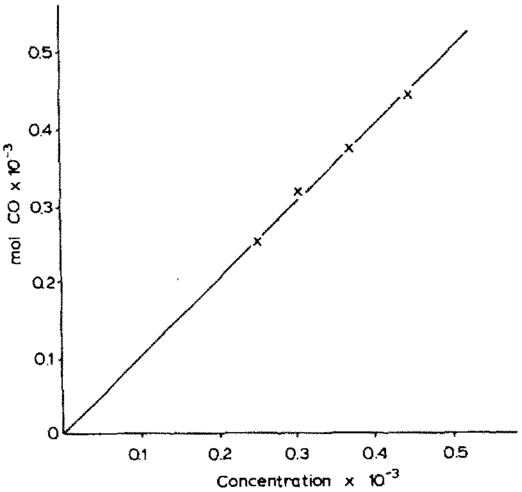


Fig. 2. CO uptake by Mn(PPhEt$_2$)Br$_2$ at 0°C using different concentrations of the complex (THF blank absorption subtracted).

TABLE 1

CHARACTERISATION DATA FOR THE COMPLEXES

| Complex | Analyses (Found (calcd.) (%)) | | | $\mu_{eff}$ [a] | $\nu$(CO) (cm$^{-1}$) |
|---|---|---|---|---|---|
| | C | H | P | | |
| $Mn(PPhMe_2)Cl_2$ | 36.6 | 4.5 | 11.7 | | |
| | (36.4) | (4.2) | (11.7) | | |
| $Mn(PPhMe_2)(CO)Cl_2$ | 37.0 | 3.6 | 10.4 | 5.80 | 2100 |
| | (36.9) | (3.8) | (10.6) | | |
| $Mn(PPhMe_2)Br_2$ | 27.3 | 3.3 | 8.8 | | |
| | (27.2) | (3.1) | (8.8) | | |
| $Mn(PPhMe_2)(CO)Br_2$ | 28.2 | 3.0 | 8.8 | 5.80 | 2100 |
| | (28.4) | (2.9) | (8.1) | | |
| $Mn(PPhMe_2)I_2$ | 22.8 | 2.6 | 6.7 | | |
| | (21.5) | (2.5) | (6.9) | | |
| $Mn(PPhMe_2)(CO)I_2$ | 22.6 | 2.4 | 6.7 | 5.75 | 2085 |
| | (22.7) | (2.3) | (6.5) | | |
| $Mn(PPhEt_2)Cl_2$ | 42.9 | 5.9 | 9.5 | | |
| | (41.1) | (5.1) | (10.6) | | |
| $Mn(PPhEt_2)(CO)Cl_2$ | 40.8 | 4.9 | 9.6 | 5.90 | 2095 |
| | (41.2) | (4.7) | (9.7) | | |
| $Mn(PPhEt_2)Br_2$ | 31.5 | 3.9 | 8.1 | | |
| | (31.6) | (4.1) | (8.2) | | |
| $Mn(PPhEt_2)(CO)Br_2$ | 32.0 | 3.9 | 7.7 | 5.80 | 2097 |
| | (32.3) | (3.7) | (7.6) | | |
| $Mn(PPr^n_3)Cl_2$ | 38.6 | 6.9 | 9.8 | | |
| | (37.8) | (7.3) | (10.8) | | |
| $Mn(PPr^n_3)(CO)Cl_2$ | 38.0 | 6.5 | 9.9 | 5.90 | 2099 |
| | (38.2) | (6.7) | (9.9) | | |
| $Mn(PPr^n_3)Br_2$ | 28.8 | 5.6 | 8.3 | | |
| | (29.0) | (5.9) | (8.5) | | |
| $Mn(PPr^n_3)(CO)Br_2$ | 29.7 | 5.3 | 7.8 | 5.85 | 2090 |
| | (29.8) | (5.2) | (7.7) | | |

[a] $\mu_B$.

drop method. Each complex was found to be capable of absorbing/desorbing CO without any sign of decomposition at 0°C (X = Cl, Br) or −40°C (X = I). The

$$MnX_2(PR_3) + CO \rightleftharpoons MnX_2(PR_3)(CO)$$

reaction was studied over 5 completely reversible cycles and the desorbed gas was shown to be carbon monoxide by mass spectral methods. Although long-term absorption/desorption cycles were not studied it appears to us that the system is a stable one and many more than 5 cycles may be possible without any decomposition of the system.

Although each complex does absorb 100 mol% CO per Mn (Fig. 3) it is apparent from plots of CO absorbed versus time that distinct plateaus do exist in the uptake curves. We are convinced that these are not artefacts of our experimental set-up, but are probably due to the formation of intermediates in the uptake process. We have previously observed such plateau in curves of dioxygen uptake by $MnX_2$ $(PBu^n_3)$ (X = Br, I) complexes, and shown that isolatable dioxygenated species exist which exhibit ESR signals significantly different from the unoxygenated $MnX_2(PBu^n_3)$

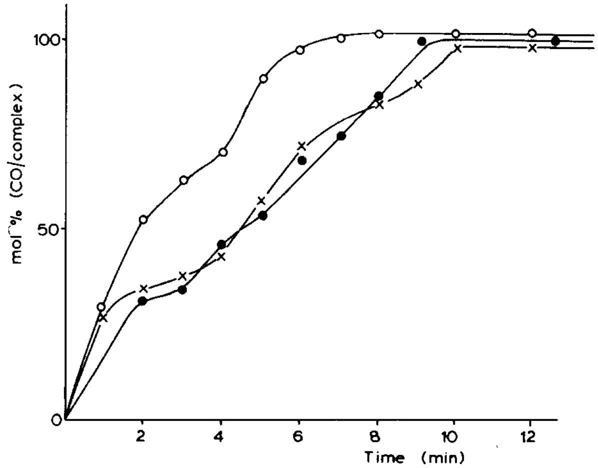
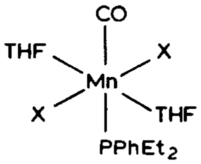


Fig. 3. Comparison of CO uptake by $Mn(PR_3)Cl_2$ complexes at 0°C in THF solution, $PR_3$ = ● $PPr^n_3$; x $PPhMe_2$; ⊙ $PPhEt_2$.

complexes [4]. Further comparison of the relative rates of uptake indicate that for the $MnLBr_2$ series the relative rate is L = $PPhMe_2 > PPhEt_2 \simeq PPr^n_3$ (Fig. 4). However, inspection of Fig. 3 will show that for the chloro series the order is $PPr^n_3 > PPhEt_2 \sim PPhMe_2$. This suggests that the rate of reaction is both halide and phosphine dependent.

The ESR spectra of $MnX_2(PR_3)(CO)$ complexes have been recorded in frozen THF glasses at 77 K (the carbonylation process was monitored by gas burette measurements to ensure 1/1 reaction has occurred). The spectra are typical of $d^5$ complexes with $S = 5/2$. The spectra of $MnX_2(PPhEt_2)(CO)$ (X = Cl, Br) are quite typical. That of $MnBr_2(PPhEt_2)(CO)$ has a strong absorption at $g \sim 6$ (1000 G) together with other absorptions at 3300, 4000, 5100 and 7200 G. The shape and position of the $g \sim 6$ signal is typical of axially symmetrical highspin $d^5$ complexes, and indicates coordination of the THF solvent. Although deduction of $\lambda$ and $D$ parameters must await $Q$-band spectra and computer simulation, the present $X$-band results do allow us to postulate a structure in solution similar to that proposed for the $Mn(PBu^n_3)(O_2)X_2$ complexes [4], i.e. a tetragonally distorted octahedral configuration:



( X = Cl, Br )

The overall appearance of the $MnBr_2(PPEt_2)(CO)$ spectrum is similar to that of $MnBr_2(PBu^n_3)(O_2)$, but the resolution of hyperfine coupling to $^{55}Mn$ on the $g \sim 6$ signal is very poor, and the positions of the remaining absorptions are slightly shifted.

Also for the $MnCl_2(PPhEt_2)(CO)$ complex, we find a general similarity in the

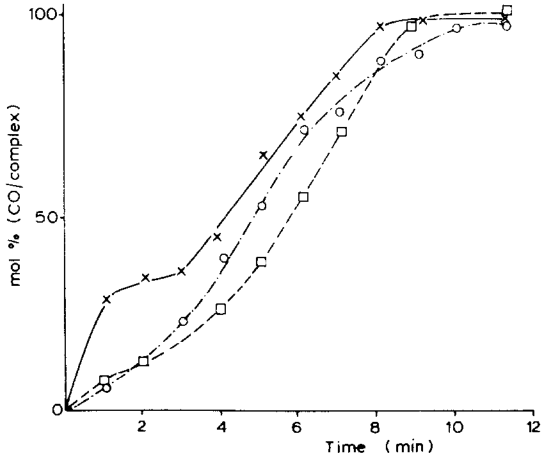


Fig. 4. Comparison of CO uptake by Mn(PR$_3$)Br$_2$ complexes at 0°C in 100 ml THF, R$_3$ =⊙ PPr$^n_3$; x PPhMe$_2$; ⊡ PPhEt$_2$.

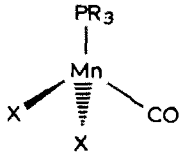
overall spectrum shape to that of MnCl$_2$(PBu$^n_3$)(O$_2$). The spectrum of the carbonyl complex exhibits a strong $g \sim 2$ signal with several poorly resolved weak absorptions in the low field region. This again leads us to propose a similar structure to that shown above.

*Solid state studies*

The carbonyl complexes are synthesised by allowing a sample of Mn(PR$_3$)X$_2$ to stand exposed to one atmosphere of dry carbon monoxide for one day or more. The completeness of the reaction may be checked by increase in weight. For example, 2.65 g of MnCl$_2$(PPhMe$_2$) will absorb carbon monoxide until the weight increase to 2.93 g; no further weight increase occurs after complete formation of MnCl$_2$(PPhMe$_2$)(CO). Once isolated the complexes may be stored indefinitely under dry carbon monoxide.

The mull infrared spectra of the MnCl$_2$(PR$_3$)(CO) complexes exhibit a strong absorption in the 2100–2085 cm$^{-1}$ region, assignable to $\nu$(CO). When compared to $\nu$(CO) of carbon monoxide gas (2141 cm$^{-1}$) it is seen that the shift to lower energy is characteristic of a fairly weak chemical bond between manganese and carbon monoxide. Typical terminal carbonyl complexes absorb at 2100–1850 cm$^{-1}$. We observe no correlation between the $\nu$(CO) values and parameters such as phosphine basicity or cone-angle, although for a given phosphine the $\nu$(CO) for the chloro and bromo derivatives is significantly higher than for the iodo derivative. The magnetic moments values lie in the range 5.75–5.90 $\mu_\beta$ and are typical of high-spin $3d^5$ species, and the values are almost identical to those found for the parent Mn(PR$_3$)X$_2$ complexes.

The solid state ESR spectrum of MnCl$_2$(PPhMe$_2$)(CO) at −150°C exhibits lines at $g \sim 4$ and $g \sim 2$, together with other lines. A similar spectrum was obtained for MnBr$_2$(PPhEt$_2$)(CO). Comparison of these spectra with the published graphs of Dowsing and Gibson [12–14] suggests that for these complexes $D$ is 0.05 and $\lambda$ is 1/3, strongly indicative of a tetrahedral structure in the solid state.



This observation is similar to that for $MnX_2(PR_3)(O_2)$ in the solid state or in non-coordinating solvents.

We have extensively studied solid state isotherms and give brief details here. When initially exposed to carbon monoxide a rapid surface absorption takes place, and the weight increase may be plotted against $p_{CO}$ to yield isotherms, e.g. Fig. 5. The uptake can be considered as a multi-step process. In the first step there is a rapid increase in weight which corresponds to the formation of a monolayer on the surface of the complex. During the second stage there is virtually no weight increase. We suggest that during this period molecular rearrangement takes place and a second set of coordination sites are generated. The third stage involves a second period of rapid weight increase and corresponds to the occupying of this second series of coordination sites. The exact nature of the structural changes which take place in the second stage of CO uptake are uncertain, but it does seem likely to involve breaking of bridging Mn–X–Mn bonds. We have identified both terminal and bridging Mn–X linkages in the infrared spectra of some of the $MnX_2(PR_3)$ complexes [3,15].

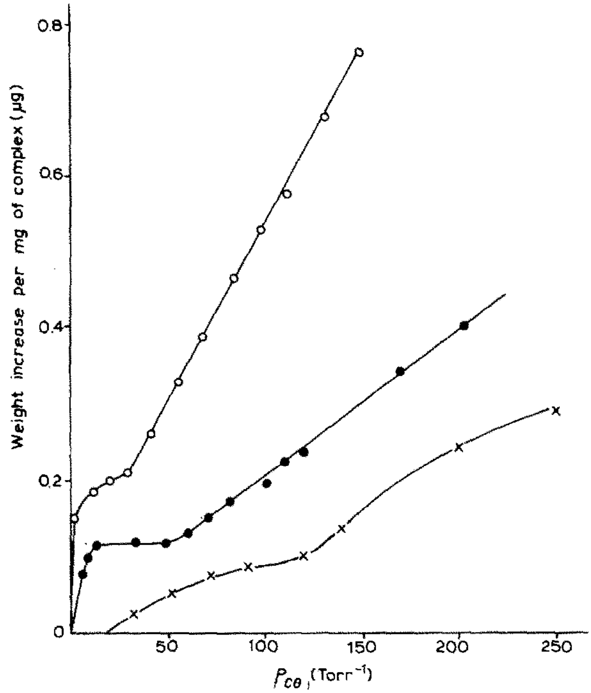


Fig. 5. Effect of the halogen in CO uptake by $Mn(PPhMe_2)X_2$ complexes in the solid state at room temperature, X = x Cl; ● Br; ⊙ I.

Figure 5 illustrates the isotherms for $Mn(PPhMe_2)X_2$ ($X = Cl$, Br, I), and it can be seen that the affinity for carbon monoxide follows the series I > Br > Cl. This is found to be the case for the complexes of the other phosphines and may reflect the ease with which the Mn–X–Mn bonds are broken (I > Br > Cl).

## Experimental

It is important to stress that all reactants and solvents should be anhydrous and scrupulous attention to this is necessary, as is the employment of inert atmosphere conditions, for the preparation of the $MnX_2(PR_3)$ complexes. The drying of materials has been described by us in great detail [16]. The failure of Green, Mingos and coworkers to prepare these simple compounds has led them to imply that they do not exist [17]. On the other hand, Skapski and Wilkinson [18] have isolated several manganese(II) phosphine complexes with a 1/1 $Mn/PR_3$ stoicheiometry.

### *Preparation of $MnX_2(PR_3)$ complexes*

The apparatus usually employed is a round bottom 250 $cm^3$ flask equipped with a side-arm containing a ground glass tap. This is dried in vacuo stored under argon, and subsequently dried by the application of a Bunsen flame prior to use. Typically the anhydrous $MnX_2$ salt (4.0 mmol) is added to the flask, the flask is evacuated, and the magnetic stirrer allowed to break up any lumps by stirring at high speed for ca. 2 h, after which general practice is to gently Bunsen flame the flask to ensure no moisture contamination has occurred during handling and transfer of the stored $MnX_2$ to the flask. (The technique of finally powdering the $MnX_2$ salt and finally warming in vacuo does appear to be beneficial to clean reaction products.) After cooling to room temperature a 60/40 mixture of freshly distilled toluene/dichloromethane (90 $cm^3$) is added after prior degassing under dinitrogen. Once in the flask a vacuum is applied and let down under argon; this is repeated three times to ensure no dioxygen is present. Prior to the addition of the phosphine (4.0 mmol) in degassed dichloromethane (35 $cm^3$) the syringe used for the addition of the solution is heated in an oven at 130°C for 2 h, allowed to cool in an argon atmosphere and flushed with argon before loading. On addition of the tertiary phosphine, application of a vacuum an return to ambient pressure under argon is carried out four times to further ensure no possibility of oxidation of the phosphine. The mixture is allowed to stir under argon at room temperature for 5 days, after which the volume of the solution is reduced to ca. 25 $cm^3$ by application of a vacuum (heat is not applied). The resulting solid is separated by Schlenk techniques under argon, allowed to dry under argon stream, taken up in dichloromethane (50 $cm^3$), filtered in a Schlenk apparatus, the volume further reduced to ca. 10 $cm^3$, and the resulting complex filtered and dried in vacuo. Yields are almost quantitative.

### *Preparation of the $MnX_2(PR_3)(CO)$ complexes*

This will be illustrated for $MnCl_2(PPhMe_2)(CO)$. The $MnCl_2(PPhMe_2)$ (2.65 g, 0.01 mol) complex was finely ground in a glove box filled with dinitrogen. It was placed in a stoppered flask and weighed. It was then placed in a glove box under a carbon monoxide atmosphere. After 24 h the sample plus flask was reweighed and the weight increase was 0.28 g, equivalent to 0.01 mol carbon monoxide uptake. (No further increase in weight occurred on standing under carbon monoxide.)

The $MnX_2(PR_3)(CO)$ complexes can be stored indefinitely under dry carbon monoxide.

*Measurement of CO uptake in solution*

The essentials of the apparatus employed are illustrated in Fig. 6. The flask containing the solution under study and the large gas reservoir bulb (G) are maintained at the same temperature by means of a large cooling bath. The remainder of the apparatus consists of a standard gas burette fitted with a three-way tap $T_1$. A typical experiment would proceed as follows:

The flask, F, is flame dried in vacuo and, upon cooling, is charged with 100 $cm^3$ of the $MnLX_2$ solution to be studied. It is then placed in the bath and connected to the rest of the apparatus via tap joint $T_2$. The gas reservoir G is then evacuated via $T_1$ and the inert gas above the solution is removed via $T_3$, tap $T_2$ is kept closed throughout this procedure. Carbon monoxide is then introduced into reservoir G and into the gas burette via $T_1$. The apparatus is usually filled to a pressure of approximately 1.1 atmospheres at 0°C. Upon cooling the gas contracts and the mercury levels A and B change. Thermal equilibrium is attained when no further gaseous contraction occurs, i.e. when A and B give a steady reading of the pressure in the apparatus (this usually takes 20–30 min). Once thermal equilibrium is attained, the uptake can be performed. Tap $T_2$ is opened and the mercury in A and B adjusted by means of the reservoir R until they are level and the initial reading on the burette is taken from level C. Under the conditions employed carbon monoxide absorption is complete after 5–10 min depending on stirrer speed and the nature of the complex. (The rate of stirring is controlled and the uptake plots are reproducible with an estimated error of ca. 5%).

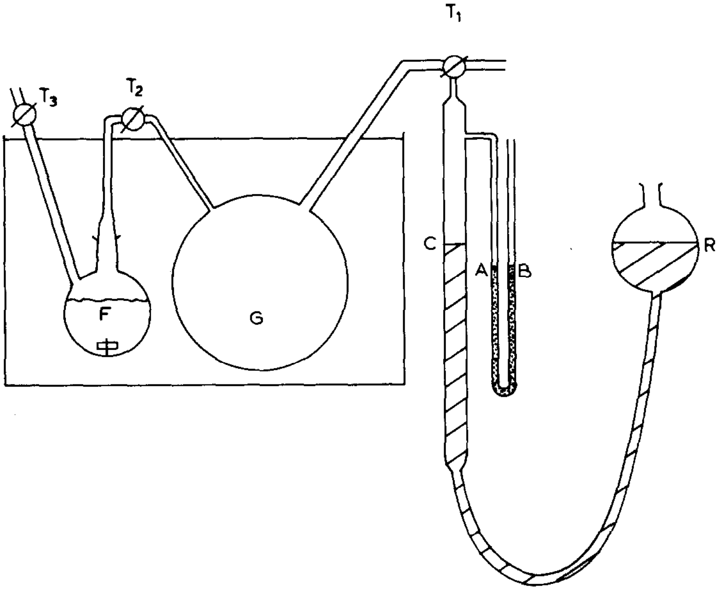


Fig. 6. Thermostated apparatus for carbon monoxide uptake measurements by the manganese(II) compounds using a gas burette.

A typical experiment using $2.8 \times 10^{-3}$ mol $MnI_2(PPhMe_2)$ in 100 $cm^3$ THF (i.e. a $2.8 \times 10^{-2}$ molar solution) resulted in the absorption of 76.0 $cm^3$ carbon monoxide at 0°C over ca. 7 min; no further carbon monoxide absorption occurred. The blank THF (100 $cm^3$) absorbs 14.1 $cm^3$ of carbon monoxide under identical conditions, resulting in 61.9 $cm^3$ $O_2$ being attributed to the reaction $MnI_2(PPhMe_2) + CO \rightarrow MnI_2(PPhMe_2)(CO)$. The 61.9 $cm^3$ $O_2$ is equivalent to 99% of the theoretical 1/1 absorption.

On removal of the flask F from the bath (tap $T_1$ closed) desorption can be examined. On warming the solution to room temperature under vacuum the carbon monoxide desorbs from solution. Any THF vapor leaving the flask was trapped out and fresh THF was added to the flask from time to time to maintain the concentration of the solution. We have been able to follow the desorption quantitively by GLC methods.

A solution of $MnI_2(PPhMe_2)$ was allowed to absorb carbon monoxide to give 100% saturation at 0°C. A vacuum was applied to the flask and it was allowed to warm to room temperature. The "dead space" in the flask and attachments was then returned to atmospheric pressure by the introduction of dinitrogen. The resultant gas mixture was then analyzed by GLC and the % composition $N_2/CO$ determined. Knowing the "dead space" volume and the % CO in the gas mixture then it is a simple matter to determine the volume of CO evolved from the solution in the desorption cycle. The calculation goes thus:

Total dead space = 184 $cm^3$

We find 33.1% CO in 184 $cm^3$ of an $CO/N_2$ sample.

$$\text{Release from solution} = 33.1/100 \times 184$$
$$= 60.9\ cm^3$$

This represents 98.4% of the absorbed CO.

*Solid state isotherms*

Absorption isotherms for $MnX_2(PR_3)_2$ complexes were obtained at ambient temperature using a Stanton-Redcroft TG-750 micro-balance which was connected to a vacuum line (Fig. 7). The system consists of a main microbalance which is connected to a two channel chart recorder to record the weight change and a vacuum line with a Pirani gauge and a pressure transducer connected to the other channel of the chart recorder to record pressure of the system and is calibrated for different pressures. The solid sample under investigation was placed on the platinum sample pan. The round bottom flask (A) was positioned and the system was evacuated for several hours by turning taps $t_1$ and $t_2$ to the vacuum. When the sample was degassed (no weight decrease was observed in the recorder and the Pirani gauge showed a steady vacuum at $10^{-2}$ Torr) $t_1$ and $t_2$ were closed and the vacuum system was filled by carbon monoxide. By careful control of the tap $t_1$, small amounts of the gas were admitted to the system and the pressure was recorded by the use of the pressure transducer (B) connected to the chart recorder. The system is left under constant pressure of the gas until a steady line was observed on the weight recorder (no further weight increase observed i.e. equilibrium point which depend on the complex, gas and the pressure under investigation; the time may differ between 5 to 40 min or more). Then another pressure of the gas was introduced to the system.

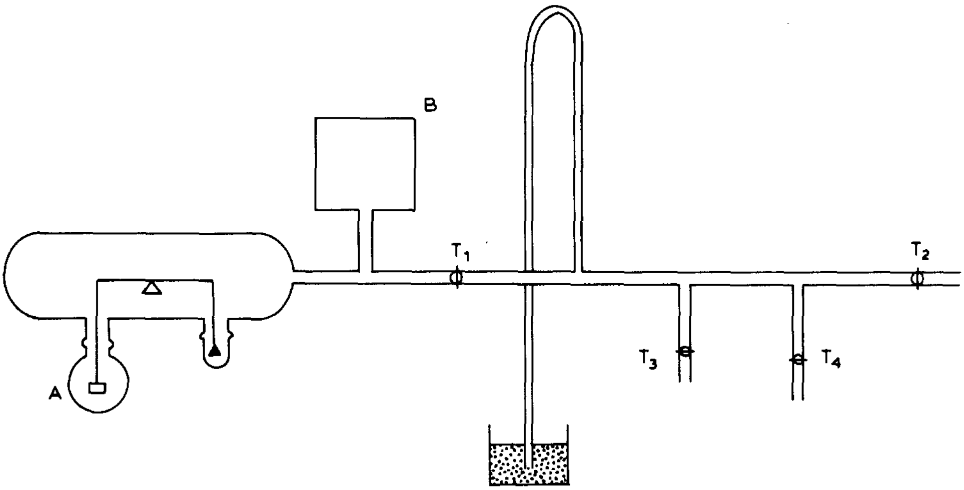


Fig. 7. Apparatus for studying absorption of carbon monoxide by the manganese(II) phosphine complexes in the solid state.

This was continued until a steady weight increase was obtained. This data was used to plot the isotherm (weight increase vs. pressure of gas) for each gas.

Blank runs were performed with empty sample pan and for the particular gases used no buoyancy correction was found to be necessary over the range of pressures used in each determination.

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